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(54) PRODUCTION OF POLYMERIZABLE TRIORGANOSILYL UNSATURATED CARBOXYLATE

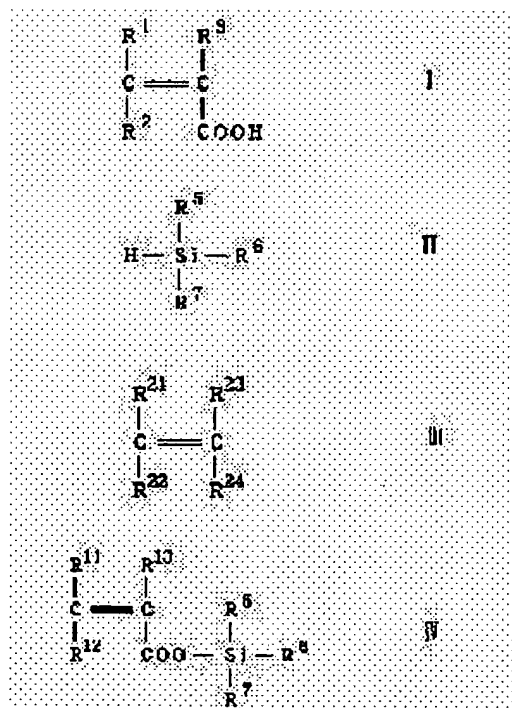
(57)Abstract:

PROBLEM TO BE SOLVED: To provide the subject high-purity compound without causing by- products in high yield by reacting an unsaturated carboxylic acid with a triorganosilane in the presence of a reducing double bond by using a dehydrogenating catalyst.

SOLUTION: An unsaturated carboxylic acid of formula I.

(R¹ and R² are each H, methyl or COOR⁴; R⁴ is H, an alkyl, an aryl, an aralkyl, etc.; R³ is H, methyl, CH₂COOR⁴, etc.) is reacted with a triorganosilane of formula II (R⁵ to R⁷ are each an alkyl, a cycloalkyl, an aryl or an aralkyl) in the presence of a compound of formula III (R²¹ and R²² are each H, methyl, aryl, etc.; R²³ is H, methyl, etc.; R²⁴ is an alkyl, an alkenyl, an aryl, etc.), and a dehydrogenating catalyst at -20 to 250°

C to give a compound of the formula (R¹¹ and R¹² are each H, methyl or COOR¹⁴; R¹⁴ is



an alkyl, an aryl, a triorganosilyl, etc.; R13 is H, methyl, CH₂COOR₁₄, etc.). No triorganosilyl saturated carboxylate as an unfavorable by-product is formed by this method.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of polymerization nature Tori ORGANO silyl partial saturation carboxylate. In more detail, polymerization nature unsaturated carboxylic acid and the Tori ORGANO silane are made to react, and it is related with the approach of manufacturing polymerization nature Tori ORGANO silyl partial saturation carboxylate.

[0002]

[Description of the Prior Art] Generally manufacture of polymerization nature Tori ORGANO partial saturation carboxylate is conventionally performed by the approach of carrying out dehydrochlorination of unsaturated carboxylic acid and the Tori ORGANO monochloro silane under existence of a base like triethylamine. However, by this approach, the process which removes the hydrogen chloride which carries out a byproduction was needed, the process became complicated, and there was a fault in which yield and purity are reduced.

[0003] On the other hand, the method of making a carboxylic acid and a hydro silane react under existence of the catalyst containing a metal or metallic compounds, such as palladium, nickel, and a rhodium, and manufacturing silyl carboxylate is learned (L.H.Sommer, J.E.Lyons, J.Am.Chem.Soc., 91, 7061 (1969)).

[0004] However, the double bond of polymerization nature unsaturated carboxylic acid is returned by the hydrogen generated during the reaction when this reaction was performed using polymerization nature unsaturated carboxylic acid and the Tori ORGANO silane (hydrogenation), and a lot of Tori ORGANO silyl saturation carboxylate generates simultaneously. Although distillation is required in order to refine polymerization nature Tori ORGANO silyl partial saturation carboxylate, since these Tori ORGANO silyl saturation carboxylate has the boiling point dramatically close to the polymerization nature Tori ORGANO silyl partial saturation carboxylate of the specified substance, purification by distillation is difficult, and it is difficult to deal in the polymerization nature Tori ORGANO silyl partial saturation carboxylate of a high grade.

[0005] Moreover, the approach of performing under existence of a palladium catalyst and a ligand by JP,4-154789,A as an approach of making unsaturated carboxylic acid and the Tori ORGANO silane reacting, and obtaining Tori ORGANO silyl partial saturation carboxylate Although the approach of performing under existence of a palladium catalyst and a nonprotic solvent is proposed in JP,4-154790,A, respectively By these approaches, there is much generation of Tori ORGANO silyl saturation carboxylate, and the polymerization nature Tori ORGANO silyl partial saturation carboxylate which is the specified substance cannot yet be sold at satisfying quality and yield.

[0006]

[Problem(s) to be Solved by the Invention] This invention makes it a technical problem to offer the approach of manufacturing the polymerization nature Tori ORGANO silyl partial saturation carboxylate which is the specified substance by the high grade and high yield, without generating the Tori ORGANO silyl saturation carboxylate which is the by-product which is not desirable in view of the fault

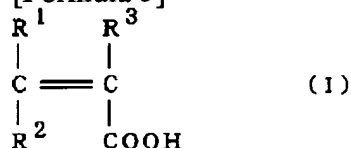
of such a Prior art.

[0007]

[Means for Solving the Problem] this invention persons resulted that polymerization nature TORI ORGANO silyl partial saturation carboxylate could be manufactured by the high grade and high yield in a header and this invention, without being accompanied by reduction of the double bond of polymerization nature unsaturated carboxylic acid, when unsaturated carboxylic acid and the TORI ORGANO silane were made to react under existence of the compound which has the double bond of reducibility using a dehydrogenation catalyst as a result of inquiring wholeheartedly, in order to attain this technical problem.

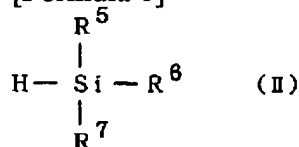
[0008] That is, this invention is (1) general-formula (I): [0009].

[Formula 5]



[0010] the inside of [type, and R1 and R2 are the same -- or -- differing -- a hydrogen atom, a methyl group, or four -COOR(s) (it is here) R4 -- a hydrogen atom, an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical -- expressing -- expressing -- R3 -- a hydrogen atom, a methyl group, or four -CH2COOR(s) (it is here) R4 -- the above -- being the same -- the unsaturated carboxylic acid which expresses and is shown by] either [at least / whose] R1 or R2 are a hydrogen atom (however, both R1 and R2 are hydrogen atoms when R3 is a methyl group or four -CH2COOR(s)), and general formula (II): [0011]

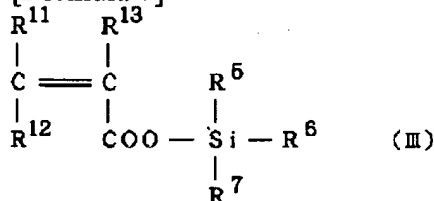
[Formula 6]



[0012] (-- the inside of a formula, and R5, R6 and R7 are the same -- or it differs and an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical is expressed --) -- the TORI ORGANO silane shown is reacted under existence of a dehydrogenation catalyst -- making -- general formula (III):

[0013]

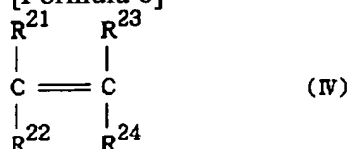
[Formula 7]



[0014] the inside of [type, and R11 and R12 are the same -- or -- differing -- a hydrogen atom, a methyl group, or 14 -COOR(s) (it is here) It expresses. the TORI organosilyl group guided from the TORI ORGANO silane R14 is indicated to be by an alkyl group, the cycloalkyl radical, the aryl group, the aralkyl radical, or said general formula (II) -- expressing -- R13 is a hydrogen atom, a methyl group, or 14 -CH2COOR(s) (it is here). R14 -- the above -- being the same -- expressing -- either [at least] R11 or R12 -- a hydrogen atom -- it is (however, when R13 is a methyl group or 14 -CH2COOR(s)) In case R5, R6, and R7 both R11 and whose R12 are hydrogen atoms manufacture the polymerization nature TORI ORGANO silyl partial saturation carboxylate shown by the same] as the above It is related with the manufacturing method of the polymerization nature TORI ORGANO silyl partial saturation carboxylate characterized by making the compound which has the double bond of reducibility live together.

[0015] further -- this invention -- (2) -- the compound which has the double bond of said reducibility -- general formula (IV): [0016]

[Formula 8]



[0017] the inside of [type, and R21 and R22 are the same -- or -- differing -- a hydrogen atom, a methyl group, an aryl group, or 25 -COOR(s) (it is here) R25 -- an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical -- expressing -- expressing -- R23 -- a hydrogen atom, a methyl group, or 25 -CH2COOR(s) (it is here) R25 -- the above -- being the same -- expressing -- R24 -- an alkyl group, an alkenyl radical, an aryl group, 26 -COOR(s), 26 -OCOR(s), or 26 -OR (it is here) It expresses. R26 -- an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical -- expressing -- Either [at least] R21 or R22 are a hydrogen atom (however, when R23 is 25 -CH2COOR(s)). both R21 and R22 are hydrogen atoms -- it is related with the manufacturing method of the polymerization nature Tori ORGANO silyl partial saturation carboxylate given [aforementioned] in (1) term which is the compound shown by].

[0018] Furthermore, this invention relates to the manufacturing method of the (3) aforementioned (1) term which is the metal chosen from the group which said dehydrogenation catalyst becomes from palladium, a rhodium, a ruthenium, and platinum, or its metallic compounds, or polymerization nature Tori ORGANO silyl partial saturation carboxylate given in (2) terms.

[0019] further -- this invention -- (4) -- said unsaturated carboxylic acid is related with the manufacturing method of polymerization nature Tori ORGANO silyl partial saturation carboxylate the above (1) which is an acrylic acid or a methacrylic acid, (2), or given in (3) terms.

[0020]

[Embodiment of the Invention] In a general formula (I), the shape of a straight chain, branched-chain un-permuting, or the permutation alkyl group of the carbon numbers 1-18, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, pentyl, hexyl, octyl, DESHIRU, lauryl, hexadecyl, and stearyl, is raised as an alkyl group shown by R4 in four -COOR(s) shown by R1 or R2. Moreover, as a cycloalkyl radical shown by R4, un-permuting or the permutation cycloalkyl radicals of carbon numbers 6-12, such as cyclohexyl, methylcyclohexyl, ethyl cyclohexyl, methoxy cyclohexyl, chloro cyclohexyl, cyclopentyl, and cyclo dodecyl, are raised. Moreover, as an aryl group shown by R4, un-permuting or the permutation aryl groups of carbon numbers 6-12, such as phenyl, tolyl, the xylyl, mesityl, ethyl phenyl, propyl phenyl, isopropyl phenyl, methoxyphenyl, phenoxyphenyl, chlorophenyl, and naphthyl, are raised. As an aralkyl radical furthermore shown by R4, un-permuting or the permutation aralkyl radicals of carbon numbers 7-14, such as benzyl, methylbenzyl, methoxybenzyl, ethoxybenzyl, phenoxy benzyl, phenylethyl, phenyl butyl, and chloro benzyl, are raised.

[0021] The unsaturated carboxylic acid shown by the general formula (I) used by this invention is a compound which has a carboxyl group and a polymerization nature partial saturation double bond in intramolecular, for example, boletic acid monoester, such as maleic-acid monoester, such as an acrylic acid, a methacrylic acid, a maleic acid, maleic-acid monomethyl, maleic-acid mono-n-butyl, maleic-acid mono-lauryl, maleic-acid mono-cyclohexyl, and maleic-acid monophenyl, boletic acid, boletic acid monomethyl, boletic acid mono-n-butyl, and boletic acid mono-benzyl, an itaconic acid, a crotonic acid, etc. are raised. Especially an acrylic acid and a methacrylic acid are useful.

[0022] In a general formula (II), the shape of a straight chain, branched-chain un-permuting, or the permutation alkyl group of the carbon numbers 1-18, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, pentyl, hexyl, octyl, DESHIRU, lauryl, and stearyl, is raised as an alkyl group shown by R5, R6, or R7. Moreover, as a cycloalkyl radical shown by R5, R6, or R7, un-permuting or the permutation cycloalkyl radicals of carbon numbers 6-12, such as cyclohexyl, methylcyclohexyl, ethyl cyclohexyl, methoxy cyclohexyl, chloro cyclohexyl, cyclopentyl, and cyclo

dodecyl, are raised. Moreover, as an aryl group shown by R5, R6, or R7, un-permuting or the permutation aryl groups of carbon numbers 6-12, such as phenyl, tolyl, the xylyl, mesityl, ethyl phenyl, propyl phenyl, isopropyl phenyl, methoxyphenyl, phenoxyphenyl, chlorophenyl, and naphthyl, are raised. As an aralkyl radical furthermore shown by R5, R6, or R7, un-permuting or the permutation aralkyl radicals of carbon numbers 7-14, such as benzyl, methylbenzyl, methoxybenzyl, ethoxybenzyl, phenoxy benzyl, phenylethyl, phenyl butyl, and chloro benzyl, are raised.

[0023] As an example of the Tori ORGANO silane expressed with the general formula (II) used by this invention For example, a trimethyl silane, a triethyl silane, a Tori n-propyl silane, A triisopropyl silane, a Tori n-butyl silane, a TORIISO butyl silane, A Tori sec-butyl silane, a Tori n-hexyl silane, a triphenyl silane, A dimethyl t-butyl silane, a dimethyl n-octyl silane, a dimethyl lauryl silane, A dimethyl stearyl silane, a dimethyl cyclohexyl silane, an ECHIRUJI n-butyl silane, An ethyl diphenyl silane, n-butyl diphenyl silane, diethyl phenylsilane, a diisopropyl n-butyl silane, n-butyl diphenyl silane, t-butyl diphenyl silane, etc. are raised.

[0024] In a general formula (III), the alkyl group shown by R14 in 14 -CH₂COOR(s) shown by R14 or R3 in 14 -COOR(s) shown by R11 or R12, the cycloalkyl radical, the aryl group, and the aralkyl radical are the same as the alkyl group shown by R4, respectively, a cycloalkyl radical, an aryl group, and an aralkyl radical.

[0025] Although it will not be restricted especially if the catalysis which causes dehydrogenation occurs as a dehydrogenation catalyst used for this invention, a metal simple substance or metallic compounds, such as palladium, a rhodium, a ruthenium, platinum, copper, cobalt, nickel, chromium, and zinc, are raised, for example. A metal simple substance can be used in the condition of could use it with gestalten, such as powder and a particle, and having made carbon, a silica, asbestos, or an alumina supporting these metals. As metallic compounds, organic-acid salts, such as inorganic-acid salts, such as halogenides, such as the oxide of these metals, a hydroxide, a cyanide, a chloride, a bromide, and an iodide, a sulfate, and a nitrate, acetate, and propionate, these metals or metallic compounds, and a coordination compound with triphenyl phosphine, a benzonitrile, triethylamine, an acetylacetone, etc. are raised. These catalysts can mix and use independent or two sorts or more. Metal simple substances, such as palladium from the point that the catalysis of dehydrogenation is excellent, a rhodium, a ruthenium, and platinum, and especially those metallic compounds are desirable.

[0026] In a general formula (IV), un-permuting or the permutation aryl groups of carbon numbers 6-12, such as phenyl, tolyl, the xylyl, mesityl, ethyl phenyl, propyl phenyl, isopropyl phenyl, methoxyphenyl, chlorophenyl, and naphthyl, are raised as an aryl group shown by R21 or R22.

[0027] Moreover, in a general formula (IV), the shape of a straight chain, branched-chain un-permuting, or the permutation alkyl group of the carbon numbers 1-18, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, pentyl, hexyl, octyl, DESHIRU, lauryl, hexadecyl, stearyl, hydroxyethyl, methoxy ethyl, and dimethylaminoethyl, is raised as an alkyl group shown by R25 in 25 -COOR(s) shown by R21 or R22. Moreover, as a cycloalkyl radical shown by R25, un-permuting or the permutation cycloalkyl radicals of carbon numbers 6-12, such as cyclohexyl, methylcyclohexyl, ethyl cyclohexyl, methoxy cyclohexyl, chloro cyclohexyl, cyclopentyl, and cyclo dodecyl, are raised.

Moreover, as an aryl group shown by R25, un-permuting or the permutation aryl groups of carbon numbers 6-12, such as phenyl, tolyl, the xylyl, mesityl, ethyl phenyl, propyl phenyl, isopropyl phenyl, methoxyphenyl, phenoxyphenyl, chlorophenyl, and naphthyl, are raised. As an aralkyl radical furthermore shown by R25, un-permuting or the permutation aralkyl radicals of carbon numbers 7-14, such as benzyl, methylbenzyl, methoxybenzyl, ethoxybenzyl, phenoxy benzyl, phenylethyl, phenyl butyl, and chloro benzyl, are raised.

[0028] Moreover, in a general formula (IV), the shape of a straight chain, branched-chain un-permuting, or the permutation alkyl group of the carbon numbers 1-18, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, pentyl, hexyl, octyl, DESHIRU, lauryl, hexadecyl, and stearyl, is raised as an alkyl group shown by R24. Moreover, as an alkenyl radical shown by R24, un-permuting or the permutation alkenyl radicals of carbon numbers 2-14, such as vinyl, 1-methylvinyl, 1-ethyl vinyl, 1-octyl vinyl, 1-lauryl vinyl, 1-phenyl vinyl, and 2-propenyl, are raised. Moreover, as an aryl group shown

by R24, un-permuting or the permutation aryl groups of carbon numbers 6-12, such as phenyl, tolyl, the xylyl, mesityl, ethyl phenyl, propyl phenyl, isopropyl phenyl, methoxyphenyl, phenoxyphenyl, chlorophenyl, and naphthyl, are raised.

[0029] moreover, as an alkyl group shown in a general formula (IV) by R26 in 26 -COOR(s) shown by R24, 26 -OCOR(s), or 26 -OR Methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, The shape of a straight chain, branched-chain un-permuting, or the permutation alkyl group of the carbon numbers 1-18, such as sec-butyl, pentyl, hexyl, octyl, DESHIRU, lauryl, hexadecyl, stearyl, hydroxyethyl, methoxy ethyl, and dimethylaminoethyl, is raised. Moreover, as a cycloalkyl radical shown by R26, un-permuting or the permutation cycloalkyl radicals of carbon numbers 6-12, such as cyclohexyl, methylcyclohexyl, ethyl cyclohexyl, methoxy cyclohexyl, chloro cyclohexyl, cyclopentyl, and cyclo dodecyl, are raised. Moreover, as an aryl group shown by R26, un-permuting or the permutation aryl groups of carbon numbers 6-12, such as phenyl, tolyl, the xylyl, mesityl, ethyl phenyl, propyl phenyl, isopropyl phenyl, methoxyphenyl, phenoxyphenyl, chlorophenyl, and naphthyl, are raised. As an aralkyl radical furthermore shown by R26, un-permuting or the permutation aralkyl radicals of carbon numbers 7-14, such as benzyl, methylbenzyl, methoxybenzyl, ethoxybenzyl, phenoxy benzyl, phenylethyl, phenyl butyl, and chloro benzyl, are raised.

[0030] As an example of a compound of having the double bond of the reducibility expressed with the general formula (IV) used by this invention For example, a methyl acrylate, an ethyl acrylate, acrylic-acid n-butyl, Acrylic-acid lauryl, acrylic-acid methoxy ethyl, a methyl methacrylate, N-butyl methacrylate, cyclohexyl methacrylate, methacrylic-acid benzyl, Acrylic ester or methacrylic ester, such as methacrylic-acid hydroxyethyl and dimethylaminoethyl methacrylate, Maleates, such as maleic-acid dimethyl and di-n-butyl maleate Fumaric-acid ester, such as dimethyl fumarate and di-n-butyl fumarate Itaconic-acid ester, such as dimethyl itaconate and itaconic-acid di-n-butyl Crotonic-acid ester, such as ethyl crotonate and crotonic-acid n-butyl Unsaturated hydrocarbon, such as vinyl ester [, such as vinyl ether, such as ethyl vinyl ether and isobutyl vinyl ether vinyl acetate, propionic-acid vinyl and butanoic acid vinyl,], styrene, stilbene, 1-butene, 1, and 3-swine JIEN, etc. is raised. In addition, as a compound which has the double bond of the reducibility which can be used by this invention, aldehydes, such as ketones, such as an acetone, a methyl ethyl ketone, and an acetylacetone, an acetaldehyde, and a propyl aldehyde, are raised. These can mix and use independent or two sorts or more.

[0031] The aforementioned unsaturated carboxylic acid, the Tori ORGANO silane, the compound that has the double bond of reducibility, and a dehydrogenation catalyst are added, and -20-250 degrees C of silyl esterification reactions by dehydrogenation are made to usually perform under the temperature of 0-180 degrees C preferably in this invention. Although this reaction is performed in the state of the solution which usually added the solvent, control of the reaction by especially trouble not having a non-solvent, either and a part of reactant being dropped is also possible.

[0032] moreover -- although the addition of the compound which has the double bond of reducibility does not have especially a limit -- one mol of the Tori ORGANO silanes -- receiving -- a 0.5 to 10 time mol -- the rate of a 0.8 to 3 time mol is preferably desirable. Moreover, as for the rate of the Tori ORGANO silane and unsaturated carboxylic acid, it is desirable to consider as the 1-3 mol equivalent of carboxyl groups of polymerization nature unsaturated carboxylic acid to one mol of the Tori ORGANO silanes.

[0033] As a solvent used for said reaction, for example Aromatic hydrocarbon system solvents, such as benzene, toluene, and a xylene, Ester solvent, such as ethyl acetate and butyl acetate, diethylether, Ether system solvents, such as a tetrahydrofuran and dioxane, a pentane, Aliphatic hydrocarbon system solvents, such as a hexane and a heptane, an acetone, a methyl ethyl ketone, Ketone solvent, such as methyl isobutyl ketone, dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, an acetonitrile, Non-proton system polar solvents, such as hexa methyl phosphoamides, N-methyl pyrrolidone, and triethylamine, A chlorinated hydrocarbon system solvent, such as alcoholic solvent, such as a methanol, ethanol, isopropyl alcohol, and a butanol, ethylene dichloride, chloroform, and a carbon tetrachloride, etc. is raised. Moreover, these solvents may be used independently, or may mix and use two or more sorts.

[0034] Moreover, in said reaction, in order to prevent a polymerization, the hydrogen which may add polymerization inhibitor, such as hydroquinone, p-methoxy phenol, 2, and 6-G t-butyl hydroxybenzene, and is generated during a reaction may blow nitrogen gas and oxygen-nitrogen mixed gas (air is also included) into reaction mixture, and may miss them out of a system.

[0035] The reaction mixture after reaction termination is processed with a conventional method, and it deals in the object compound of this invention. For example, a catalyst is carried out a ** exception and it distills after condensing filtrate. Thus, polymerization nature Tori ORGANO silyl partial saturation carboxylate is obtained by high yield and the high grade, and even if most Tori ORGANO silyl saturation carboxylate like the conventional example is not contained or is contained, it is dramatically slight.

[0036]

[Example] An example and the example of a comparison explain this invention concretely below. About purity, and partial saturation/saturation ratio (weight ratio), it measured by the gas chromatography. Partial saturation/saturation ratio is weight ratios of the Tori ORGANO silyl partial saturation carboxylate which is the object compound of this invention, and the Tori ORGANO silyl saturation carboxylate to which the double bond was returned. Yield is the yield based on the used Tori ORGANO silane.

[0037] the flask equipped with example 1 thermometer, the agitator, and the reflux condenser -- Tori n-butyl silane 100.2g (0.5 mols), 47.3g [of methacrylic acids] (it is 1.1 time mol to 0.55-mol and silane), and p-methoxy phenol 0.2g, 56.0g [of vinyl acetate] (it is 1.3 time mol to 0.65-mol and silane), and acetonitrile 60g -- adding -- further -- as a catalyst -- 2.0g of 1% palladium-carbon -- in addition, it be made to react at 80 degrees C for 5 hours Reaction mixture was cooled after that, it distilled after condensing filtrate except for the catalyst by filtration, and Tori n-butylsilyl methacrylate 118.2g (b. p.114-117 degrees C / 3mmHg, 88.0% of yield, 98.0% of purity) was obtained. Partial saturation/saturation ratio = it was 98.5/1.5.

[0038] the same equipment as example 2 example 1 -- triisopropyl silane 79.2g (0.5 mols), 47.3g [of methacrylic acids] (it is 1.1 time mol to 0.55-mol and silane), and p-methoxy phenol 0.2g, 64.4g [of methyl acrylates] (it is 1.5 time mol to 0.75-mol and silane), and dimethylformamide 60g -- adding -- 2.0g of 1 more% palladium-carbon -- in addition, it was made to react at 100 degrees C for 5 hours Reaction mixture was cooled after that, it distilled after condensing filtrate except for the catalyst by filtration, and triisopropyl silyl methacrylate 102.7g (b. p.110-112 degrees C / 10mmHg, 90.7% of yield, 98.6% of purity) was obtained. Partial saturation/saturation ratio = it was 100/0.

[0039] To the same equipment as example 3 example 1, t-butyl diphenyl silane 120.1(0.5 mols) g, 47.3g (it is a 1.1 time mol to 0.55 mols and a silane) of methacrylic acids, p-methoxy phenol 0.2g, styrene 108.8g (1.05 mols) The mol was added 2.1 times to the silane, tris (triphenylphosphine) chloro rhodium 1.0g was further added as mixture and a catalyst (toluene 45g and dimethylformamide 15g) as a solvent, and it was made to react at 90 degrees C for 5 hours. Reaction mixture was cooled after that, it distilled after condensing filtrate except for the catalyst by filtration, and diphenyl t-butylsilyl methacrylate 138.0g (b. p.158-160 degrees C / 0.6mmHg, 90.3% of yield, 98.3% of purity) was obtained. Partial saturation/saturation ratio = it was 100/0.

[0040] According to the blending ratio of coal of a table 1, taught the compound and solvent which have the double bond of the Tori ORGANO silane, unsaturated carboxylic acid, a dehydrogenation catalyst, polymerization inhibitor, and reducibility to the same equipment as four to example 7 example 1, it was made to react to it on condition that table 1 publication, and polymerization nature Tori ORGANO silyl partial saturation carboxylate was obtained. A result is shown in a table 1.

[0041]

[A table 1]

表 1

実施例	トリオルガノシラン (g)	不飽和カルボン酸 (g)	脱水素触媒 (g)	還元性不飽和化合物 (g)	重合禁止剤 (g)	溶媒 (g)	反応温度／反応時間	収量 (g)	収率 (%)	純度 (%)	不飽和／飽和比
4	トリn-ブチルシラン 100.2 (0.5モル)	アクリル酸 39.6 (0.55モル)	1%パラジウム-炭素 1.0	酢酸ビニル 56.0 (0.65モル)	p-メトキシフェノール 0.2	アセトニトリル 60	80℃／12時間	123.1	91.0	97.4	98.2／1.8
5	ジイソプロピルジフェニルシラン 120.2 (0.5モル)	メタクリル酸 47.3 (0.55モル)	トリス(トリフェニルフォスフィン)クロロロジウム 0.5	イソブチルビニルエーテル 56.0 (0.58モル)	ハイドロキノン 0.2	トルエン 120	90℃／5時間	145.2	95.0	98.0	100／0
6	ジイソプロピルn-ブチルシラン 86.1 (0.5モル)	メタクリル酸 43.2 (0.5モル)	塩化白金酸 0.3	アクリル酸エチル 60.0 (0.6モル)	p-メトキシフェノール 0.2	ベンゼン 300	80℃／8時間	108.7	90.5	98.5	100／0
7	トリイソプロピルシラン 79.2 (0.5モル)	マレイン酸モノメチル 71.5 (0.6モル)	0.7%パラジウム-炭素 3.6	マレイン酸ジメチル 86.0 (0.42モル)	p-メトキシフェノール 0.2	酢酸エチル 60 ジメチルホルムアミド 40	80℃／5時間	115.0	85.0	97.7	98.5／1.5

[0042] Tori n-butyl silane 100.2g, 47.3g [of methacrylic acids], and p-methoxy phenol 0.2g, dimethylformamide 60g, and 1.0g of 1% palladium-carbon were added to the same equipment as example of comparison 1 example 1, and it heated at 100 degrees C for 5 hours. an after that catalyst -- a ** exception -- carrying out -- after condensing filtrate -- distilling -- Tori n-butylsilyl methacrylate 123.5g[-- b. -- p. 112 - 116-degree-C / 3mmHg, and 87.0% [of yield] (saturated compound is included)] was obtained. Purity was 70.2% and was partial saturation / saturation ratio =70.7/29.3. Recovery (yield except a saturated compound) was 61.5%.

[0043] Diisopropyl n-butyl silane 86.2g, 43.2g [of acrylic acids], and hydroquinone 0.2g, toluene 100g, and tris (triphenylphosphine) chloro rhodium 0.5g were added to the same equipment as example of comparison 2 example 1, and it heated at 100 degrees C for 5 hours. an after that catalyst -- a ** exception -- carrying out -- after condensing filtrate -- distilling -- diisopropyl n-butylsilyl acrylate 107.4g[-- b. -- p. 102 - 104-degree-C / 3mmHg, and 85.0% [of yield]] was obtained. Purity was 55.6% and was partial saturation / saturation ratio =56.7/43.3. Recovery (yield except a saturated compound) was 48.2%.

[0044]

[Effect of the Invention] The polymerization nature Tori ORGANO silyl partial saturation carboxylate which is the specified substance can be sold at a high grade and high yield, without generating the Tori ORGANO silyl saturation carboxylate which is the by-product which is not desirable according to the approach of this invention.

[Translation done.]

* NOTICES *

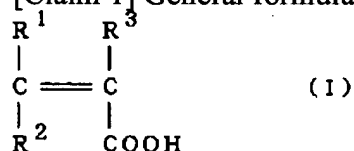
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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

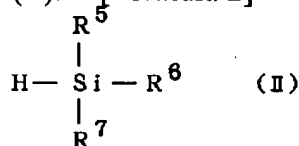
CLAIMS

[Claim(s)]

[Claim 1] General formula (I): [Formula 1]

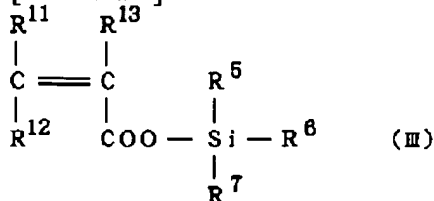


the inside of [type, and R1 and R2 are the same -- or -- differing -- a hydrogen atom, a methyl group, or four -COOR(s) (it is here) R4 -- a hydrogen atom, an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical -- expressing -- expressing -- R3 -- a hydrogen atom, a methyl group, or four -CH2COOR(s) (it is here) R4 -- the above -- being the same -- the unsaturated carboxylic acid which expresses and is shown by] either [at least / whose] R1 or R2 are a hydrogen atom (however, both R1 and R2 are hydrogen atoms when R3 is a methyl group or four -CH2COOR(s)), and general formula (II): -- [Formula 2]



(-- the inside of a formula, and R5, R6 and R7 are the same -- or it differs and an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical is expressed --) -- the Tori ORGANO silane shown is reacted under existence of a dehydrogenation catalyst -- making -- general formula (III): --

[Formula 3]

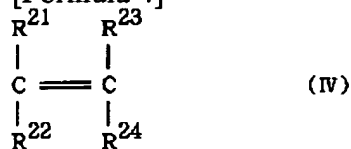


the inside of [type, and R11 and R12 are the same -- or -- differing -- a hydrogen atom, a methyl group, or 14 -COOR(s) (it is here) It expresses. the Tori organosilyl group guided from the Tori ORGANO silane R14 is indicated to be by an alkyl group, the cycloalkyl radical, the aryl group, the aralkyl radical, or said general formula (II) -- expressing -- R13 is a hydrogen atom, a methyl group, or 14 -CH2COOR(s) (it is here). R14 -- the above -- being the same -- expressing -- either [at least] R11 or R12 -- a hydrogen atom -- it is (however, when R13 is a methyl group or 14 -CH2COOR(s)) In case R5, R6, and R7 both R11 and whose R12 are hydrogen atoms manufacture the polymerization nature Tori ORGANO silyl partial saturation carboxylate shown by the same] as the above The manufacturing method of the

polymerization nature Tori ORGANO silyl partial saturation carboxylate characterized by making the compound which has the double bond of reducibility live together.

[Claim 2] the compound which has the double bond of said reducibility -- general formula (IV): --

[Formula 4]



the inside of [type, and R21 and R22 are the same -- or -- differing -- a hydrogen atom, a methyl group, an aryl group, or 25 -COOR(s) (it is here) R25 -- an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical -- expressing -- expressing -- R23 -- a hydrogen atom, a methyl group, or 25 -CH2COOR(s) (it is here) R25 -- the above -- being the same -- expressing -- R24 -- an alkyl group, an alkenyl radical, an aryl group, 26 -COOR(s), 26 -OCOR(s), or 26 -OR (it is here) It expresses. R26 -- an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical -- expressing -- Either [at least]. R21 or R22 are the manufacturing method of the polymerization nature Tori ORGANO silyl partial saturation carboxylate according to claim 1 which is the compound shown by] which is a hydrogen atom (however, both R21 and R22 are hydrogen atoms when R23 is 25 -CH2COOR(s)).

[Claim 3] The manufacturing method of the polymerization nature Tori ORGANO silyl partial saturation carboxylate according to claim 1 or 2 which is the metal chosen from the group which said dehydrogenation catalyst becomes from palladium, a rhodium, a ruthenium, and platinum, or its metallic compounds.

[Claim 4] The manufacturing method of the polymerization nature Tori ORGANO silyl partial saturation carboxylate according to claim 1, 2, or 3 said whose unsaturated carboxylic acid is an acrylic acid or a methacrylic acid.

[Translation done.]